

*Supplementary Materials*

## **Elucidating the Influence of Electric Fields toward CO<sub>2</sub> Activation on YSZ (111)**

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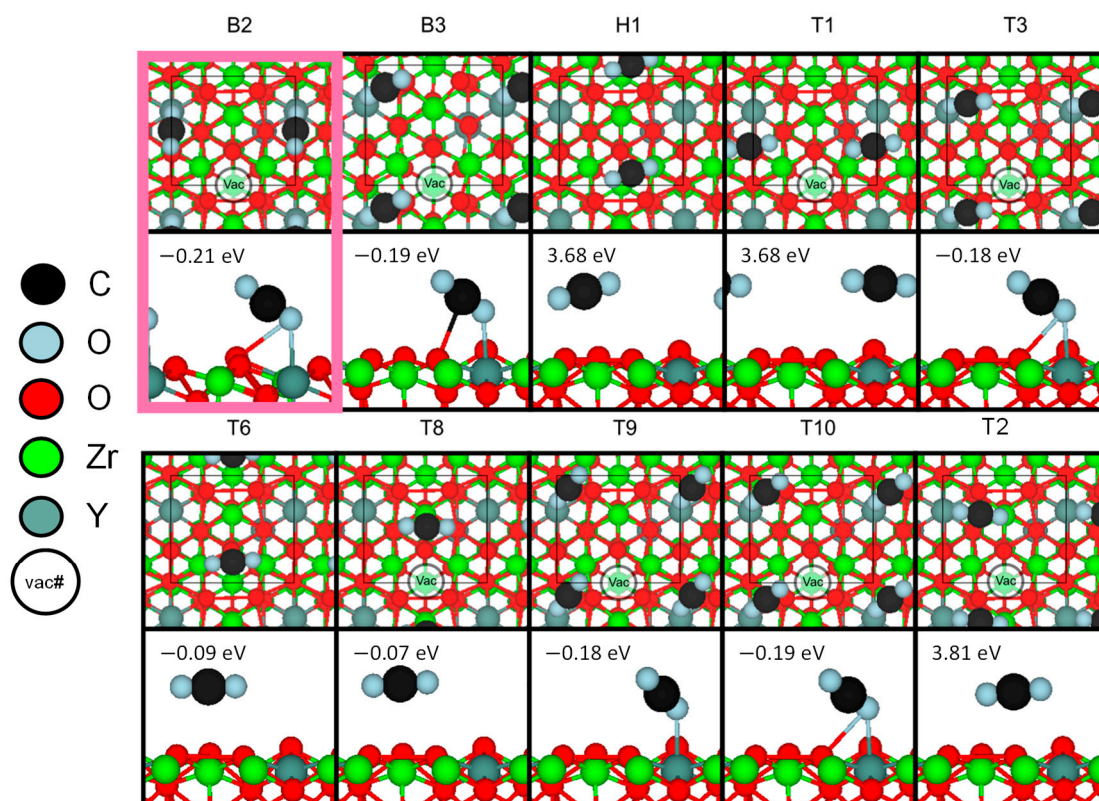
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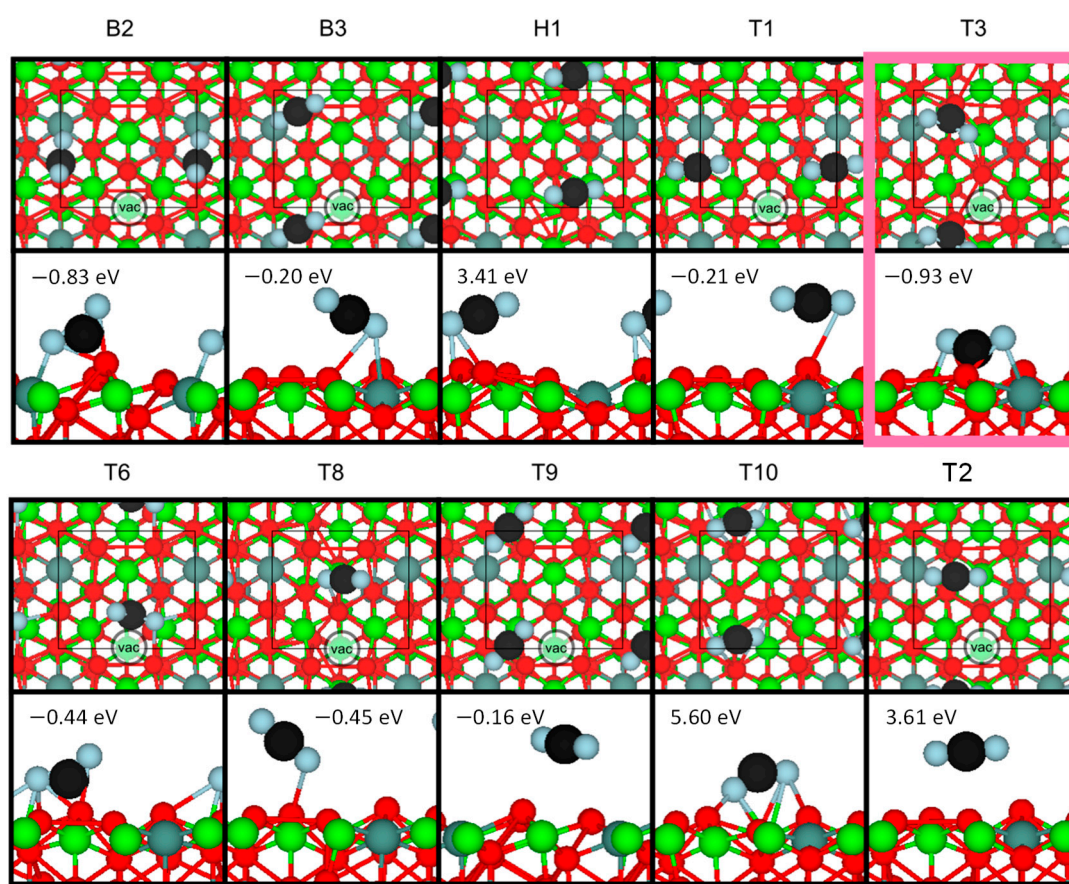
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The adsorption energetics of CO<sub>2</sub> was determined on all distinct adsorption sites on YSZ (111) for three electric field cases: 0, -1, and +1 V/Å. As shown in Figure S1, the very weak attractive interaction between CO<sub>2</sub> and YSZ (111) occurs within the vicinity of the Y-cation (sites B2, T3, B3, T9, and T10) in the absence of an electric field, where a weak dipole–dipole interaction occurs. As such, it is quite unlikely that the adsorption of CO<sub>2</sub> will occur.



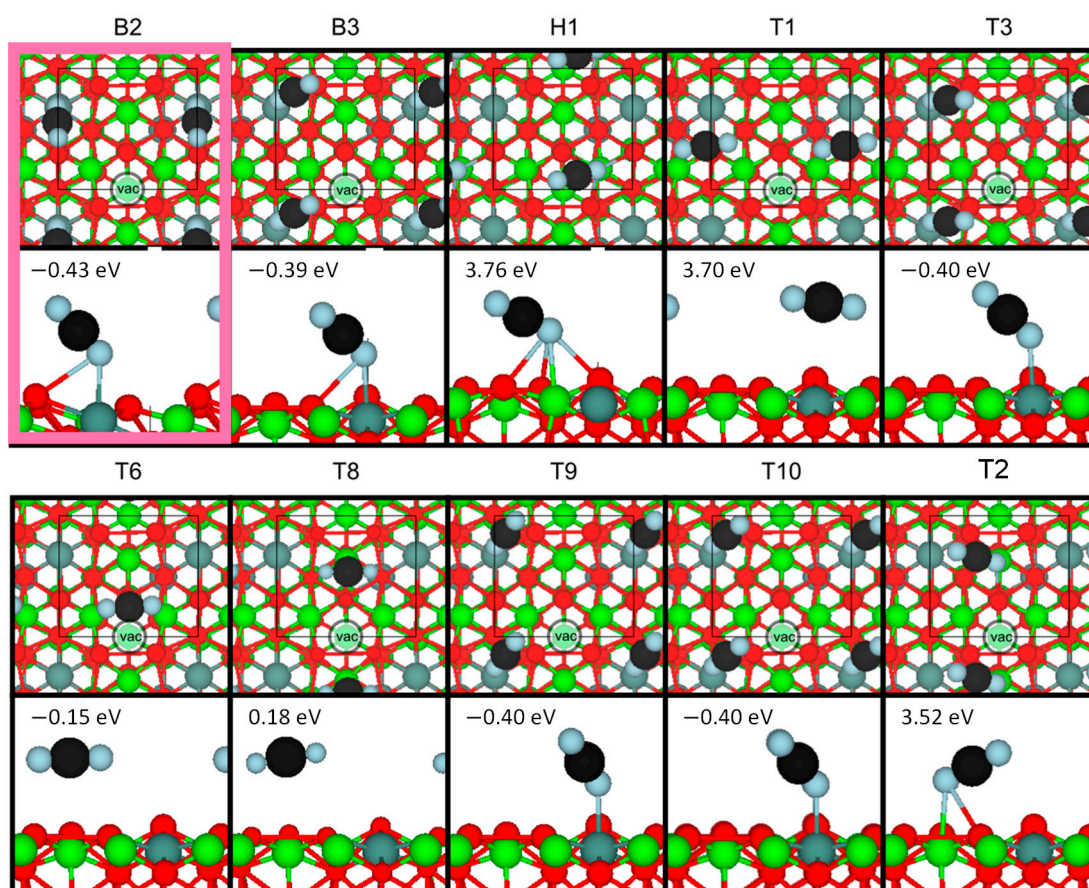
**Figure S1.** Comparison of CO<sub>2</sub> adsorption sites and their corresponding adsorption energies on YSZ (111) in the absence of an electric field. Highlighted in pink is the most favorable adsorption site.

When a  $-1$  V/Å external electric field was applied, CO<sub>2</sub> was chemisorbed on sites T3, B2, and T6, as shown in Figure S2. Interestingly, while the strongest interaction continued to occur within the vicinity of the Y-cations (T3 and B2), chemisorption within the vicinity of a Zr-cation was also possible, as shown in Site T6. We hypothesize that the generally stronger interaction occurs due to the charge accumulation on the surface ions. The highly positive adsorption energies shown in Site H1 and Site T10 indicate that adsorption on these sites is an endothermic process and are the least likely occurring sites.



**Figure S2.** Comparison of CO<sub>2</sub> adsorption sites and their corresponding adsorption energies on YSZ (111) when a  $-1 \text{ V/\AA}$  external electric field is applied. Highlighted in pink is the most favorable adsorption site. The legend for each species is shown in Figure S1.

The comparison of adsorption energies under the  $+1 \text{ V/\AA}$  field is shown in Figure S3. We generally do not see configurational changes of CO<sub>2</sub> with respect to the  $0 \text{ V/\AA}$  case, although the adsorption energies are relatively stronger within the vicinity of the Y-cation.



**Figure S3.** Comparison between the CO<sub>2</sub> adsorption sites and their corresponding adsorption energies on YSZ (111) when a +1 V/Å external electric field is applied. Highlighted in pink is the most favorable adsorption site. The legend for each species is shown in Figure S1.